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# THEORY OF SMALL METAL CLUSTERS, FILMS, AND WIRES

## Final Report

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# ABSTRACT

The proposed work for this period was directed at the analysis of the effective Coulomb U* for metal clusters with a student and the generalization to transition-metal systems of our theory of Coulomb effects in f-shell metals. The study of U* for clusters was completed, and pursuit of the problem further did not seem warranted. The initial generalization of the theory of Coulomb effects was also completed and applied to the experiments by Ulrich Gradmann and coworkers in Clausthal, Germany. That theory is being published together with the experiment. These calculations explain an increase in moment for atoms at surfaces, steps, or kinks in steps on metal surfaces. The theory was then generalized, with the inclusion of exchange as well as the Coulomb repulsion, and the evaluation of the total energy. The aim was determination of the nature of the ground state - localized or nonlocalized and the number of occupied resonances if localized. The corresponding electronic structure provides the basis for the understanding of virtually all of the properties of these systems, including the spin-dependent scattering which presumably gives rise to giant magnetoresistance. This analysis was essentially complete at the end of the tenure of the grant and preliminary application was made to transition-metal impurities in copper.

During this period we also presented a paper, *Structural stability and interatomic interactions in covalent systems* , at the International Conference on the Physics of Semiconductors in Thessaloniki Greece, and an invited paper, *Elements of the electronic structure of interfaces*, at the APS March meeting in 1991, both based earlier work supported by ONR.

## SUMMARY OF STUDIES

### Effective U* for Clusters

A Physics graduate student, Wentau Pan, undertook in autumn quarter of 1990 the study of the effective Coulomb shift U* for a small metal cluster on a semiconductor surface, as a preliminary step in the study of such clusters. For a spherical cluster of radius $r_s$ in vacuum this would be $U^* = e^2/r_s$. If the cluster were imbedded in a semiconductor of dielectric constant $\varepsilon$, it would be $U^* = e^2/\varepsilon r_s$ and if it were a sizable distance $z$ from a semiinfinite dielectric it would be $U^* = e^2/r_s - (\varepsilon-1)e^2/(2z(\varepsilon+1))$, with the correction coming from an image charge. Pan succeeded in making evaluations for intermediate situations, showing how the charge in the cluster becomes concentrated toward the interface, but it did not prove very instructive otherwise. By mutual agreement she shifted to an assistantship with S. Doniach.

## Transition-Metal States and Localization

My own efforts were directed at the more general question of magnetism and localization in transition-metal systems, based upon my earlier treatment of f-shell metals[1]. There has been intense theoretical activity in this connection at many institutions during the present year and much of it has impacted my own approach. A seminal study in this regard has been the work of Svane and Gunnarsson[2], who introduced the Self-Interaction Correction (SIC). This approach recognizes that Density Functional Theory introduces a direct interaction of each electron with itself and an exchange interaction of each electron with itself. These two fictional terms exactly cancel in Hartree-Fock, but fail to do so in a very serious way in Local Density Theory. Svane and Gunnarsson therefore correct Local Density Theory for these self-interaction corrections in a systematic way. This is precisely the same physics - in my view - as my treatment of f-shell metals which omitted the self-interactions from the start.

Our approach[1], which considerably predates the SIC, requires extra features in order to describe the Kondo resonance, but it gives the very same picture of individually localized electronic states in the ground state of the system and very simply and quickly yields approximately the same numerical results for the ground-state properties. It was thus appropriate to generalize my f-shell method to transition-metal bands. This was quite straightforward. We define scattering phase shifts $\delta^{\pm}$ for occupied (indicated with a +) and empty (indicated with a - ) d-states on each transition metal, which have a resonant form, rising from 0 to $\pi$ over an energy range $\Gamma$ near the corresponding d-state energies $\varepsilon_d^{\pm}$. The value at the Fermi energy $\xi$ is given by

$$\tan\delta^{\pm}(\xi) = \frac{\Gamma/2}{\varepsilon_d^{\pm} - \xi} \quad . \tag{1}$$

The number of d-electrons localized at the atom may be written in terms of these phase shifts as

$$Z_d^* = 6\delta^-/\pi + 4\delta^+/\pi \tag{2}$$

for iron for example where one expects $Z_d = 6$ resonances to be occupied. The energy of the occupied state then depends upon the number of other occupied states,

$$\varepsilon_d^- = \varepsilon_d(0) + (Z_d^* - 1)U \tag{3}$$

and the energy of the empty state is

$$\varepsilon_d{}^+ = \varepsilon_d(0) + Z_d{}^*U . \qquad (4)$$

The Fermi energy was initially taken midway between these.

The results of such an analysis became very relevant to the interpretation of experiments by Ulrich Gradmann, who visited Stanford this year from Clausthal. He and coworkers had found that the magnetic moment of iron atoms, as observed by torque measurements, were larger when the atoms were at steps, or at kinks in steps, on the metal surface. This finding is quite consistent with our picture of magnetism based upon localization described above. The width of the resonance $\Gamma$ arises from interactions between neighboring d-states and is expected to vary as the square root of the number of neighbors[1]. With fewer neighbors, $\Gamma/2U$ is smaller and the net moment, given by

$$\mu = (10-Z_d)(\delta^- - \delta^+)\mu_B \qquad (5)$$

(for the case $Z_d > 5$) should be increased. We made this quantitative by solving the above equations, as a function only of the ratio of band width to Coulomb shift, $\Gamma/2U$ . We therefore solved the above equations (for $Z_d = 6$) to obtain $\mu$ as a function of $\Gamma/2U$. This curve necessarily gives $\mu/\mu_B$ equal to four at $\Gamma/2U = 0$ and it was found to drop to zero at $\Gamma/2U = 0.295$. Taking values of $\Gamma$ and $U$ from our previous publications, or from other estimates, gave values of $\Gamma/2U$ running from 0.1 to 0.2 corresponding to values of $\mu/\mu_B$ between 2.7 and 3.5, higher than the observed moment of 2.2. For interpreting the experiments, we adjusted the $\Gamma/2U$ to 0.224 to give the observed bulk moment, and scaled the value as the square root of the number of nearest neighbors for surface and edge atoms to give direct predictions of the moments. These predictions were $\mu/\mu_B = 2.95$ for the (110) surface atoms and $\mu/\mu_B = 3.4$ for step edges, compared with experimental values of 2.9-3.1 and 3.3 , respectively. This remarkable account of the experiments was presented at the International Conference on Magnetism in Edinburgh in September 1991[3] and a full account was submitted for publication in Europhysics Letters.[4]

Subsequent to this treatment of the surface properties we began a systematic application of the theory to all elements of the 3d series and to atoms of these elements dissolved in the noble metals. This constitutes a major reformulation of the electronic structure of transition-metal systems, a reformulation which corrects what appear to be major failures in the local-spin-density theory which is currently standard. In that reformulation we added several new features which were not present in the first reformulation. These are:

1) We noted that the resonance width $\Gamma$ depends upon the energy $E_d = h^2k_d^2/2m$ of the resonance according to

$$\Gamma = 0.1214 \; \frac{h^2k_d^2r_d^3}{m} \quad , \tag{6}$$

with $r_d$ the d-state radius which we have previously tabulated[5] for all elements. Thus the width of empty and full resonances were different and we incorporated that in the calculation.

2) We allowed the average energy of the resonances to shift, with the shift to be evaluated self-consistently.

3) An important feature missing in this simplest theory of localization is the exchange interaction between electrons in different d-states on the same atom. The corresponding parameter is $U_x$ and is the parameter which determines the change in energy in a free atom when the spin of an electron in the d-shell is flipped.[5] This is in contrast to our Coulomb parameter $U$ which determines the change in energy when an electron is moved from the d-shell to the s-shell in the free atom. $U_x$ is an order of magnitude smaller than $U$, but is the parameter which forces Hund's rule that the electrons in a particular shell have parallel spins a far as is allowed by the Pauli Principle. In our first generalization, we simply included its qualitative influence in producing Hund's rule. However, it could be important quantitatively in determining the nature of the ground state. For example, it shifts the relative energy of the iron state with six resonances below the Fermi energy and that with five resonances below the Fermi energy. We added the effects of $U_x$ to the calculation.

4) We evaluated the total energy of the system in terms of the self-consistently determined parameters and could therefore compare the energy of the different states for each element, which we could not do earlier.

This formulation was completed, and a program written which made the appropriate evaluations, by the end of the Grant tenure. We made application to the states of transition-metal atoms dissolved in copper, which is relevant to giant magnetoresistance. These are preliminary, but illustrative of what we can learn from such analyses. The results are listed in Table I. For each element dissolved in copper, $Z_d$ gives the number of resonances below the Fermi energy in the state with the lowest total energy. One of the states considered was an unsplit state, as would be obtained from an ordinary band calculation. In fact, such a state was found lowest for vanadium, with the unsplit resonance lying above the Fermi energy. Similarly, the resonance was found to be

TABLE I. Total energies of metal impurities in copper, $\varepsilon_{TOT}(Z_d)$ in eV per impurity, for which nonzero local moments are found (plus Cr and V). $Z_d$ is the number of occupied resonances in the ground state. Energies are relative to an imbedded atom with $Z-2$ electrons in d-states uncoupled to the free electrons and the remaining two electrons free. The energies are also given for states with one more or one less resonance and the minimum energy for an unsplit resonance $\varepsilon_{TOT}(10)$.

| | $Z_d$ | $\varepsilon_{TOT}(Z_d-1)$ | $\varepsilon_{TOT}(Z_d)$ | $\varepsilon_{TOT}(Z_d+1)$ | $\varepsilon_{TOT}(10)$ \ |
|---|---|---|---|---|---|
| $_{23}$V | 0 | | Does not split. | | -12.27 |
| $_{24}$Cr | 3 | -8.65 | -9.33 | -9.32 | -6.24 |
| $_{25}$Mn | 5 | | -6.67 | | -3.11 |
| $_{26}$Fe | 5 | | -5.09 | | -0.96 |
| $_{27}$Co | 7 | -1.94 | -2.70 | -1.86 | 0.69 |
| $_{28}$Ni | 8 | 1.11 | 0.40 | 0.87 | 2.09 |
| $_{29}$Cu | 10 | | Does not split. | | 3.50 |

unsplit in copper. Both of those predictions are correct and the corresponding atoms show no moment experimentally. Moments are predicted for the other elements and are believed to occur in all but nickel. Thus the theory appears to yield an incorrect ground state for nickel, a fact which will need to be explored. The theory suggests that in both manganese and iron there are five resonances occupied, all of the same spin, in the ground state with the resonances of the opposite spin unoccupied. It is interesting

that if correct, the ground state in iron differs from the weak-coupling limit of six occupied resonances, which we assumed in our studies in Refs. 3 and 4. If these predictions are correct, the ground state is qualitatively as represented in the local-spin-density theory of these systems. These results are preliminary, but one may see the kind of insight which they may be able to provide concerning these systems as impurities or in the pure materials.

These calculations provide a description of the electronic structure of this system, approximate as it is, and therefore predictions of virtually all of the properties of the system. For example, the total energy of the ground state is listed under $\varepsilon_{TOT}(Z_d)$, and so also are the total energies with one more or less resonance occupied. The differences are predictions of optical absorption energies in transferring electrons out of or into the d-shell, neglecting the effects of overlap which produce the Kondo peaks. The phase shifts resulting from the calculation also provide predictions of the spin-dependent scattering, and of the magnetic moment (though there are corrections arising from spin-orbit

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splitting). Whether or not they provide in the end reliable predictions of the nature of the ground state, they should at least provide an understandable way of systematizing the electronic structure and properties of transition-metal systems. Under the successor grant we are pursuing that goal.

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